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MAY 81 D F SHRIVER, B L PAPKE, M A RATNER

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STRUCTURE AND ION TRANSPORT IN POLYMER-SALT COMPLEXES

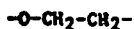
D.F. Shriver^a, B.L. Hapke^a, M.A. Ratner^a, R. Dupon^a, T. Wong^b, and M. Brodwin^b

^aDepartment of Chemistry, ^bDepartment of Electrical Engineering, and
^{a,b}Materials Research Center
Northwestern University, Evanston, IL 60201 U.S.A.

Polymer electrolytes based on alkali metal complexes of polyethers and cross-linked polyethers have significant cation mobility, which appears to arise from large-amplitude motions of the polymer. High chain flexibility not only promotes ion transport but it also is important for the initial formation of polymer-salt complexes. Several new polymer electrolyte systems are discussed which contain flexible polymer backbones and high concentrations of polar groups.

INTRODUCTION

The synthesis and characterization (1-4) of solvent-free alkali metal complexes of poly(ethylene oxide), PEO (1), prompted detailed electrical measurements with the thought that these materials might prove to be useful electrolytes for high energy density batteries (5,6). One potential advantage of polymer electrolytes is that they should conform to solid electrodes throughout charging and discharging cycles, and therefore facilitate the development of new high energy density solid state batteries. There are many fundamental aspects of polymer electrolytes which are ripe for investigation: the chemical variables which influence electrolyte formation, the relationships between structure of the polymer electrolytes and ion transport, and the detailed mechanisms for ion transport. This paper surveys accomplishments in the field of polymer electrolytes, with an emphasis on polymer-salt complex formation and ion transport mechanisms as revealed by the comparison of various response properties of the polymer electrolytes. This account will not cover any of the solvent swollen polymer electrolytes, such as traditional ion exchangers or solvent containing polymer membranes (7,8).



(1)

Poly(ethylene oxide)

POLYMER-SALT COMPLEX FORMATION

Simple ethers and short-chain polyethers are well known as solvents for alkali metal salts, and cyclic ethers (crown ethers) are effective complexing agents for alkali metal cations. Furthermore, complex formation between high molecular weight polyethers and alkali metal salts is known to occur in methanol solution (3). In all of these cases the dominant interaction is the coordination of ether oxygen

atoms to alkali metal cations. The formation of solid polyether salt complexes fits well into this general pattern.

If we make the approximation that entropic factors, polymer reorganization energies, and residual cation-anion coulombic energies are constant for the formation of the various polymer salt complexes, for any given polyether and any given cation the formation of complexes should closely correlate with lattice energies of the alkali metal salts. As shown in Table 1, this type of correlation does have general validity, since complex formation is restricted to the salts of a particular cation which are below a threshold lattice energy. In keeping with this generalization, the lowest lattice energies and the highest propensities toward complex formation are found for alkali metal salts having large anions, such as I^- , ClO_4^- , and $SO_3CF_3^-$.

The stoichiometry of polymer-salt complex formation cannot be defined with the precision characteristic of the phase relationships for most simple inorganic systems. Nevertheless, an approximate limiting stoichiometry around 4 moles of polyether oxygen per mole of alkali metal salt is observed for many of the polymer-salt interactions (1,5,8). Recent research in our laboratory provides a number of examples in which higher salt concentrations are possible, such as PEO-3.5NaBH₄. This higher salt concentration may arise from the partial filling of the coordination sphere of the Na⁺ by tight ion pairing with the BH₄⁻ anion. Evidence for such ion pairing is available from both conductivity and spectroscopic measurements (9). By contrast, the Na[B(C₆H₅)₄] complexes with PEO which we have prepared to date have on the order of 7:1 ratio of ether oxygens to alkali metal ion. Presumably, in this case the bulk of the counter ion, B(C₆H₅)₄⁻, prohibits the formation of complexes with higher concentrations of salt.

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Table 1. Comparison of PEO-Salt Complex Formation with Lattice Energies of the Pure Salts.^{a,b}

	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
F ⁻	No 1036	No 923	No 821	No 785	No 740
Cl ⁻	Yes 853	No 786	No 715	No 689	No 659
CH ₃ COO ⁻	- 881	No 763	- 682	- 656	- (682)
NO ₃ ⁻	- 848	No 756	- 687	- 658	No 625
NO ₂ ⁻	- -	No 748	- 664	- 765	- (598)
Br ⁻	Yes 807	Yes 747	No 682	No 660	No 631
N ₃ ⁻	- 818	No 731	- 658	- 632	- 604
BH ₄ ⁻	- (778)	Yes (703)	- (665)	- (548)	- (628)
I ⁻	Yes 757	Yes 704	? 644	No 630	No 604
SCN ⁻	Yes 807	Yes 682	Yes 616	Yes 619	Yes 568
ClO ₄ ⁻	Yes 723	Yes 648	- 602	- 582	- 542
CF ₃ SO ₃ ⁻	Yes (725)	Yes (650)	Yes (605)	Yes (585)	Yes (550)
BF ₄ ⁻	Yes (699)	Yes 619	- 631	- 605	- (556)
BPh ₄ ⁻	Yes (700)	Yes (630)	Yes (630)	Yes (600)	Yes (550)

^aNo = no solvent free complex formed; Yes = solvent free complex formed; Values in parentheses are either theoretical or estimated lattice energies.

^bComplex formation data is from reference (8) or the present work. Lattice energies are in kJ/mole from Jenkins, H.D.B. and Waddington, T.C., as quoted in The CRC Handbook of Chemistry and Physics, volume 61, Chemical Rubber Publishing Co., Cleveland Ohio, 1980-81.

One attractive method for the preparation of complexes having the maximum salt concentration is the exposure of a polymer film to a saturated solution of the salt in a solvent in which the pure polymer and the complex are insoluble.

This method will in principle lead to the thermodynamically stable polymer complex of maximum salt content, providing that the polymer is not swollen by the solvent and that the relaxation of the polymer chains is complete. Other methods for complex formation include the removal of solvent from a solution containing the polymer salt complex (1,5), and dissolving fine particles of the salt in the solid or the molten polymer.

As research on polymer electrolytes progresses toward more precise determinations of electrical properties, greater attention will have to be paid to the influence of impurities. Commercial polymers often contain significant concentrations of impurities, such as catalyst residues and water. For example, poly(ethylene oxide) contains several per cent of inorganic impurities, the majority of which can be removed by passage of an aqueous solution of the polymer through a mixed bed ion exchange column (10). In addition, the PEO salt complexes are hygroscopic, with the lithium salt complexes being particularly so. Water has been shown to have a large influence on the electrical properties of some lithium complexes (11), therefore systematic control and monitoring of water content is important. Infrared spectroscopic detection of the broad and intense water features around the 3,300 and 1,600 cm⁻¹ regions provides a sensitive probe for the presence of adventitious water.

NEW POLYMER-SALT COMPLEXES

Poly(propylene oxide) and poly(epichlorohydrin) have received attention as host polymers for alkali metal salts. As with poly(ethylene oxide), all of these systems are based on a backbone of ether oxygens separated by two-carbon moieties (structures I, II, and III).



(II)

(III)

Poly(epichlorohydrin)

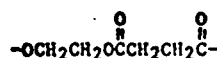
Poly(propylene oxide)

Samples of (III), which have been investigated in Armand's laboratory, and (II), which have been investigated in ours, were commercial atactic materials which produce amorphous complexes. Experiments with stereoregular analogues of these materials should provide useful clues to the steric factors which govern polymer-salt electrolyte formation. With the possible exception of poly(epichlorohydrin) the polyethers are attractive because they should exhibit a high degree of chemical inertness. The experimental situation with respect to the stability of the polyether electrolytes is unsettled. Armand observed a 4V stability range for PEO-Na[SO₃CF₃] (12) and he reported that the PEO-LiI electrolyte is stable to Li as judged by cyclic voltammetry (8), whereas Archer and Armstrong present some evidence for the formation of a resistive layer at the Li-

electrolyte interface (13). The exclusion and monitoring of impurities such as N_2 (which forms a nitride with Li) and H_2O will be particularly important in the determination of the stability of these electrolytes.

A set of general polymer attributes which should be conducive to polymer-salt complex formation is presented here, slightly modified from the original form (10): 1. The polymer should have a high concentration of polar groups, which will effectively solvate the cation and/or anion. 2. The polymer backbone should be highly flexible to permit polymer reorganization and cation solvation. 3. In general the polymer should have a low cohesive energy density to produce a favorable free energy change upon polymer-salt interaction. Factors 2 and 3 are associated with properties such as low glass transition temperatures, T_g , and low melting points.

Potentially effective polar groups for polymer electrolytes are suggested by the functional groups found in polar organic solvents such as sulfones, sulfoxides, nitriles, esters, amides, amines, imines, ketones, and sulfides. Unfortunately most of these groups are more electrochemically active than ether linkages. Initial results from studies in our laboratory on new host materials containing some of these polar groups have produced encouraging indications that many new polymer electrolytes may be prepared. The most thoroughly studied new polymer host is poly(ethylene succinate), IV, which has been found to form complexes with $Li[BF_4]$, $Li[CF_3CO_2]$, $Li[SO_3CF_3]$, and $Na[SO_3CF_3]$.



(IV)

Poly(ethylene succinate)

Complexes having 2:1 polymer repeat units per formula unit of salt have been prepared and there are good indications that higher salt concentrations can be achieved. Conductivities on the order of $1.3 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ were obtained for the $Li[BF_4]$ salt at 41°C . A quite different series of complexes was prepared from poly(ethylene sulfide), V, or poly(propylene sulfide), VI, with silver salts such as $Ag[NO_3]$ and $Ag[SO_3CF_3]$. The 5:1 poly(ethylene sulfide)- $Ag[SO_3CF_3]$ complex displayed a conductivity of about $4.6 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 65°C .



(V)

Poly(ethylene sulfide)



(VI)

Poly(propylene sulfide)

An interesting new approach to polymeric conductors is the use of cross-linked networks of low molecular weight poly(ethylene oxide) into which a salt is introduced (14,15). The intent with these materials is to achieve a combination of good mechanical and electrical properties.

STRUCTURE OF POLYETHER SALT COMPLEXES

The structures of pure poly(ethylene oxide) and of a $HgCl_2$ -PEO complex are known from X-ray structure determinations combined with vibrational spectroscopy (16,17). The pure polymer consists of an extended helix, having a fiber repeat distance of 19.48 Å, and the mercuric chloride complex consists of a zigzag polymer backbone with oxygen atoms coordinated to mercury. A similarly detailed X-ray analysis of the alkali metal salt complexes of PEO has not been carried out. In their original work on the PEO complex with KSCN, Fenton, Parker, and Wright determined an X-ray fiber repeat distance of 8.1 Å (1). More recent detailed infrared and Raman spectroscopic data have revealed several structural features (10). Mid-infrared data indicate that the OCH_2-CH_2O moieties assume a gauche conformation. Raman data in a similar frequency range provide evidence for a symmetrical breathing mode characteristic of O_n-Na stretching motion, and the far-infrared displays bands which are characteristic of translational modes for alkali metal ions in a solvent cage. Significantly, these latter features scale approximately as the square root of the mass of the alkali metal ion and are independent of the nature of most anions. A structural model which is consistent with these vibrational data and the X-ray fiber repeat distance is a sequence of trans(CC-OC), trans(CO-CC), gauche(OC-CO), trans(CC-OC), trans(CO-CC), and gauche-minus(OC-CO) conformations. This results in a helical configuration having an interior channel lined with ether oxygen atoms, and large enough to accommodate a K^+ ion (10). A view down this helical tunnel is given in Figure 1. The anions appear

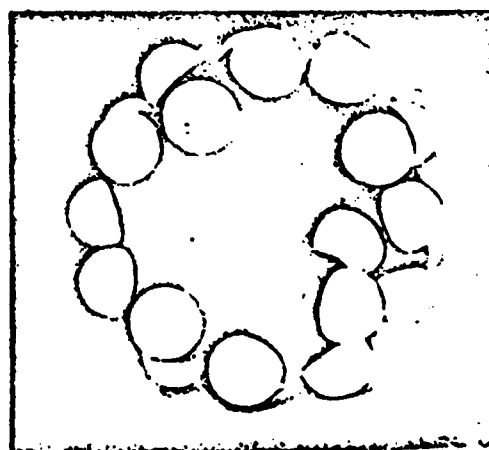


Figure 1. View down the axis of the proposed helical configuration for the PEO backbone in its complexes with sodium salts.

to lie outside the helix, with no direct cation-anion contact in most cases. The lack of crystallinity for the rubidium and cesium salt complexes is consistent with this model because the helical channel is too small to accommodate these cations.

A double helix of intertwined PEO chains has been proposed to accommodate recent estimates of the unit cell dimensions for PEO-NaSCN obtained from X-ray diffraction on oriented polycrystalline material (18). This particular model, however, places some of the $\text{OCH}_2\text{-CH}_2\text{O}$ groups in a nearly eclipsed configuration which would suffer from unfavorable repulsion of non-bonded atoms. The structures of polymers are always difficult to determine and these complex systems are particularly so.

CONDUCTIVITY AND ION TRANSPORT MECHANISMS

Transference number measurements at 23.5°C for PEO-NaSCN demonstrate that $t(\text{Na}^+)$ is very close to 1.0 (19), and unpublished NMR results indicate that $t(\text{Li}^+) > 0.95$ for a polyether lithium electrolyte (8). In addition, a variety of evidence indicates that anions have finite but very small mobilities in these materials. For example, complexes can be formed from solid salt plus solid polymer and conversely a second, salt phase can be observed to form below the melting range of some salt-rich complexes.

The simplest temperature dependent conductivities are exhibited by highly crystalline complexes such as those between sodium salts and PEO. The early reports on these materials gave two linear segments in the $\log \sigma$ vs $1/T$ plots (2,20). Recently independent research in two laboratories has demonstrated that the two-slope behavior disappears when the conductivity experiments are performed on fully complexed materials (9,18). The break observed in the original reports on the low salt materials is close to the melting temperature range of PEO, and the interpretation which we prefer is that this break is associated with the melting of residual pure or lightly doped PEO.

The non-crystalline polymer electrolytes such as those of poly(propylene oxide) alkali metal salts or PEO with rubidium or cesium salts, display curved $\log \sigma$ vs $1/T$ behavior (21). The empirical Vogel-Tamman-Fulcher equation, 1, which describes transport properties in viscous media, appears to fit the temperature dependence of the ionic conductivity very well (21).

$$\sigma = \frac{A}{\sqrt{T}} \exp\left(\frac{-B}{T-T_0}\right) \quad (1)$$

In this equation A , B , and T_0 are empirical constants, with T_0 corresponding fairly closely to the glass transition temperature, T_g , of the polymer complex. This functional dependence may be described by a model in which motion of the polymer chain is crucial for the ion transport

process. From energetic considerations it appears most likely that the cation moves without breaking many cation-oxygen interactions (22). Thus large amplitude polymer segment motions coupled with the breaking and making of one or possibly two cation-oxygen interactions per cation provides a means of cation transport which is quite unlike the hopping mechanism commonly observed for simple inorganic electrolytes. The importance of the glass transition temperature, and therefore the polymer segmental motion, has been demonstrated experimentally for the polyurethane-type polyether network complexes (23), for which the glass transition temperature can be varied widely. There is a clear indication that a fruitful approach to increased ion mobility in polymer electrolytes is to seek systems in which T_g is as low as possible.

Even though linear $\log \sigma$ vs $1/T$ plots are obtained for crystalline polymer complexes, such as PEO with lithium, sodium, and potassium salts, it appears likely that polymer motions are strongly coupled to the ion transport process in these materials as well. Microwave measurements indicate that the highly crystalline complexes exhibit strong conductive response in the GHz region which is comparable to that of pure PEO (24) and this response is attributed to high frequency segmental motion of the polymer backbone. Below 1 MHz the ion containing polymer has much higher conductivity than the pure polymer, Figure 2. This observation affords evidence that in the crystalline PEO salt complexes the low frequency ion motion is assisted by higher frequency polymer motion.

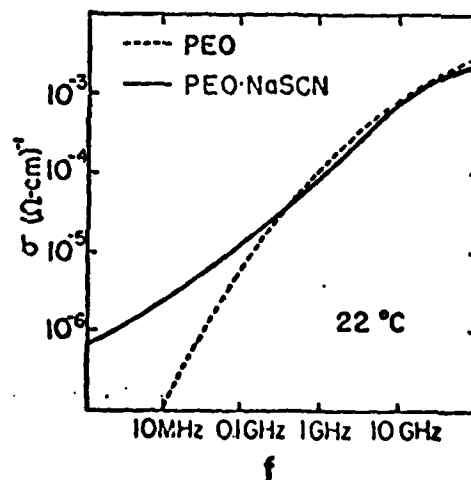


Figure 2. Variable frequency conductivity of pure PEO --- and 4.5PEO-NaSCN —.

One outstanding problem is the effect of polymer orientation on conductivity. As yet there have been no reports of systematic conductivity measurements on oriented polymer electrolytes. Our understanding of the ion transport mechanisms also would be improved by information on the volume of activation for ion transport, which will require the measurement of conductivities under hydrostatic pressures. Some pressure dependent polymer electrolyte conductivity data have been reported under nonhydrostatic conditions (25).

CONCLUSIONS

The field of polymer electrolytes has developed rapidly. Quantitative microscopic theories for ion transport mechanisms in these materials are not yet available, but some qualitative concepts with predictive value have emerged. Of the currently known systems, perhaps the most promising for room temperature battery electrolytes are the lightly cross-linked polyethers, for which the required low T_g can be fairly readily attained. It was recently estimated that a polyether with $T_g = -80^\circ\text{C}$ should display a conductivity in the 10^{-3} to 10^{-4} range at room temperature (23). This is sufficiently high to offer considerable incentive for further research on these materials.

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REFERENCES

- [1] Fenton, D.E., Parker, J.M., and Wright, P.V., Complexes of alkali metal ions with poly(ethylene oxide), *Polymer* 14 (1973) 589.
- [2] Wright, P.V., Electrical conductivity in ionic complexes of poly(ethylene oxide) *Br. Polym. J.* 7 (1975) 319-327.
- [3] Lustberg, R.D., Bailey, F.E., Jr., and Child, R.W., Interaction of inorganic salts with poly(ethylene oxide), *J. Polymer Sci. A-1*, 4 (1966) 1563-1577.
- [4] James, D.B., Stein, R.S. and Macknight, W.L., Crystallization studies of poly(ethylene oxide) metal salt complexes, *Bull. Am. Phys. Soc.* 24 (1979) 479.
- [5] Armand, M., Chabagno, J.M., and Duclot, M., Polymer solid electrolytes, Second International Meeting on Solid Electrolytes, St. Andrews, Scotland, 1978, Abstract 6.5.
- [6] Owe, J., Lloyd-Williams, S.C., Jags, G., Spurlens, P.C. and Steele, R.G.H., Transport of ions across solid electrolyte/electrode interfaces, Proceedings of the workshop on lithium nonaqueous battery electrochemistry, June 4-6, 1980, The Electrochemical Society (1980) 293-312.
- [7] Feuillade, G. and Perche, Ph., Ion conductive macromolecular gels and membranes for lithium cells, *J. Appl. Electrochem.* 5 (1975) 63-69.
- [8] Armand, M.B., Polymer electrolytes: conductivity and stability domain, Proceedings of the workshop on lithium nonaqueous battery electrochemistry, June 4-6, 1980, The Electrochemical Society, 1980, pp. 261-270.
- [9] Papke, B.L., Dupon, R., Ratner, M.A. and Shriver, D.F., Ion-Pairing in polyether solid electrolytes and its influence on ion transport, Proceedings of Fast Ion Transport in Solids Conference, Gatlinburg, TN, May 1981.
- [10] Papke, B.L., Ratner, M.A. and Shriver, D.F., Vibrational spectroscopy and structure of polymer electrolytes, poly(ethylene oxide) complexes of alkali metal salts, *J. Phys. Chem. Solids*, in press.
- [11] Farrington, G., private communication, 1981.
- [12] Armand, M.B., Duclot, M.J. and Rigaud, Ph., Polymer solid electrolytes: stability domain, Proceedings of the Third International Meeting on Solid Electrolytes; solid state ionic and galvanic cells, Tokyo, Japan, Sept. 1980.
- [13] Archer, W.I. and Armstrong, R.D., Stability of some Li^+ conducting polymeric solid electrolytes in the presence of lithium electrodes, *Electrochim. Acta* 26 (1981) 167.
- [14] Cheradame, H., Souquet, J.L., and Latour, J.M., Ionic conductivity of macromolecular networks. I. Polyether filled with sodium tetraphenylboride, *Mat. Res. Bull.* 15 (1980) 1173-1177.
- [15] Andre, D., LeNest, L.F., and Cheradame, H., Ionic conductivity of macromolecular networks. II. Networks of nitrocellulose and polyethers filled with sodium tetraphenylboride, *European Polymer J.* 17 (1981) 57-61.
- [16] Takahashi, Y. and Tadokoro, H., Structural studies of polyethers $((\text{CH}_2)_m\text{O})_n$ X. Crystal structure of poly(ethylene oxide) *Macromol.* 6 (1973) 672-675.
- [17] Iwamoto, R., Saito, Y., Ishihara, H. and Tadokoro, H., Structure of poly(ethylene oxide) complexes. II. Poly(ethylene oxide)-mercuric chloride complex, *J. Poly. Sci. A-2*, 6 (1968) 1509-1525.
- [18] Wright, P.V., private communication (1981).
- [19] Dupon, R., Whitmore, D.H. and Shriver, D.F., Transference number measurements for the polymer electrolyte poly(ethylene oxide)- NaSCN , *J. Electrochem. Soc.* 128 (1981) 715-717.
- [20] Wright, P.V., An anomalous transition to a lower activation energy for d.c. electrical conduction above the glass transition temperature, *J. Poly. Sci.* 14 (1976) 955-957.
- [21] Armand, M.B., Chabagno, J.M., and Duclot, M.J.K., Poly-ethers as solid electrolytes, in *Fast Ion Transport in Solids*, eds.

- Vashishta, P.M., Mundy, J.N., and Shenoy, G.K., North-Holland 1979, 131-136.
- [22] Papke, B.L., Shriver, D.F., and Ratner, M.A., manuscript in preparation.
- [23] Killis, A., LeNest, J.F. and Cheradame, H., Experimental evidence of the importance of the glass transition temperature on the ionic conductivity of macromolecular networks, Makromol. Chem. Rapid Communications, 1 (1980) 595-598.
- [24] Kong, T., Brodwin, M., Papke, B.L. and Shriver, D.F., Dielectric and conductivity spectra of polyethylene oxide complexes of sodium salts, Proceedings of Fast Ion Transport in Solids Conference, Gatlinburg, TN, May 1981.
- [25] Archer, W.I. and Armstrong, R.D., The effect of pressure on the a.c. impedance of a polymeric solid electrolyte, Electrochim. Acta 25 (1980) 1689-1690.

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